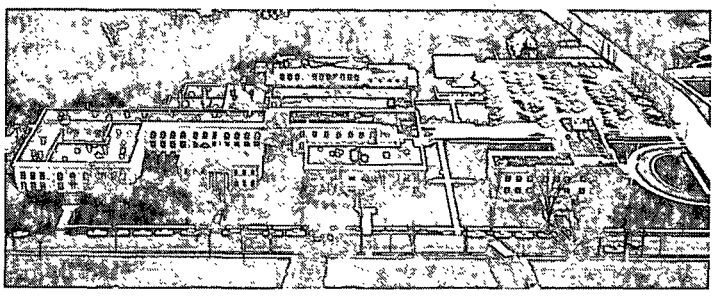

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INSOLUBLE LIGNIN MODELS (3): PREPARATION OF A POLYMER-BOUND GUAIACYLPROPANOL MODEL

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INSOLUBLE LIGNIN MODELS (3): PREPARATION OF A POLYMER-BOUND GUAIACYLPROPANOL MODEL

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ABSTRACT

A ligninlike monomer, guaiacylpropanol (**4**), has been attached at the gamma carbon through a benzyl ether linkage to a macroreticular polystyrene resin. The phenolic site of **4** was protected as an allyl ether when coupled to the resin. The loading of accessible model was determined by cleaving the benzyl ether linkage with iodotrimethylsilane (ITS) and quantifying the amount of released **4**. The ITS method was reproducible but not quantitative due to a high model loading (1.29 mmol/g). Both FTIR and ^{13}C-NMR were used to characterize the insoluble model.

INTRODUCTION

Recent work in our laboratory has centered on preparing, characterizing, and conducting simulated pulping experiments on polymer-supported lignin and carbohydrate models. The lignin[1] and carbohydrate[2] models were attached to a polystyrene support via trityl ether and benzyl ether linkages, respectively. The trityl ether linkage was subsequently found to be unstable under simulated pulping conditions;[1] the benzyl ether linkage, however, appeared to be relatively

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stable.[2, 3] The work presented herein describes our efforts at preparing and characterizing a supported ligninlike monomer, guaiacylpropanol (4), which is attached to a macroreticular polystyrene resin through the more stable benzyl ether linkage. A following paper[4] discusses the results of a study aimed at comparing the relative condensation rates of the heterogeneous model with a soluble species, syringyl alcohol, versus that of an analogous but completely soluble system.

RESULTS AND DISCUSSION

Functionalization of the Polymer Support

Macroreticular polystyrene, like lignin, is a crosslinked aliphatic-aromatic polymer. The heterogeneous model network will resemble lignin more closely in terms of its polyelectrolyte behavior if the resin has a high local concentration of ionizable lignin model units. An objective of this research was to prepare a resin with a high degree of lignin model functionalization.

The polymeric support used in previous studies in this laboratory[1, 2] has been Amberlite XE-305. Macroreticular resins of this type consist of agglomerates of microgels as shown in Figure 1.[5] The macropores, or interstices between the microgels, are accessible to all solvents. The average diameter of the macroporous network in Amberlite XE-305 is 1400 Å.[6] Unlike the macropores, the interior regions of the microgel particles are accessible only in the presence of a good swelling agent. Amberlite XE-305, due to its light crosslinking (3-4%), swells in good organic solvents, a feature which is quite useful in synthesis.[7] Previous results have shown the resin to be stable in 2.5M alkali at 170 °C for five days.[2]

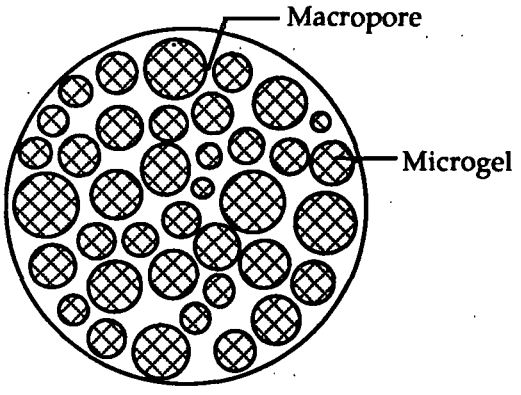


Figure 1. Cross-sectional view of a macroreticular polystyrene resin.[5]

A second macroreticular resin (Biobead SM-16) was also investigated for potential use. Table 1 compares the physical properties of the Amberlite XE-305 to those of the SM-16. As shown, the SM-16 is more highly crosslinked, which imparts limited swelling. A much smaller pore diameter (144 Å) results in the larger specific surface area (860 m^2/g). It was envisioned that the SM-16 would provide a support that had a large concentration of attached model on the outer edges of the resin thus making them more accessible to alkaline pulping reagents.

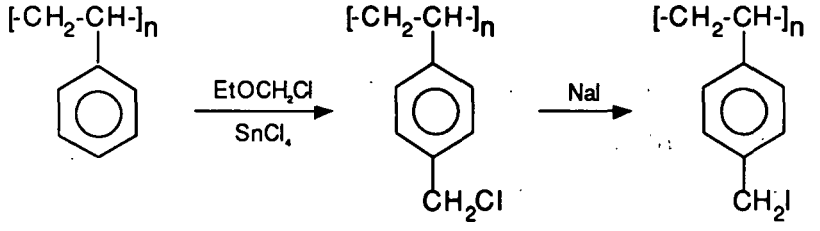
Table 1. Physical characteristics of polymeric supports.[6, 8]

	Amberlite XE-305	Biobead SM-16
Cross-link Ratio (%)	3-4	16
Ave. Pore Diam. (Å)	1400	144
Surface Area (m^2/g)	48	860
Swellability	Good	Limited

After being washed to remove surface impurities,[9] the two resins (**1**) were functionalized to benzyl iodides (Scheme 1). The iodides (**3**), which were prepared according to the Finkelstein reac-

tion[10, 11] from the corresponding chlorides (2),[12] were sought to give greater S_N2 reactivity[13] during subsequent reactions. As shown in Scheme 1, para substitution is the dominant position of chloromethylation.[14] Elemental analyses of the various benzyl halide preparations are given in Table 2.

Scheme 1



1 2 3

Depending on the catalyst and reaction conditions, several side reactions can occur during chloromethylation.[15-17] The most prominent are substitution at the backbone of the polymer or at the ortho position of the phenyl ring. Additional crosslinking can occur between the benzyl chloride residues and neighboring phenyl rings in the presence of a Lewis acid catalyst; cationic polymerization of unreacted vinyl groups has also been observed. The extent of crosslinking can be reduced by using pure grades of materials and good swelling solvents.[18, 19]

Concerning the SM-16 resin, Table 2 shows that the conversion from the chloride to the iodide is not quantitative; a second halide exchange reaction had no effect. The incomplete exchange could be due to vinyl chloride formation during the chloromethylation procedure or to limited reagent accessibility, since acetone is not a good

resin swelling solvent. Vinyl groups are more prevalent in highly crosslinked resins due to incomplete polymerization. The resulting vinyl chlorides are less reactive toward further modifications than are the aromatic chloromethyl groups.[15]

Table 2. Elemental analyses of the functionalized polystyrenes.[a]

	C	H	O	Cl	I	mmol/g[e]
Amberlite XE-305	91.25	7.67	1.64	------	------	------
PBnCl	75.56	6.65	2.16	16.30	------	4.60
PBnCl [b]	76.90	6.61	2.11	14.78	------	4.17
PBnI	54.47	4.62	1.48	0.00	39.24	3.09
PBnI [b]	63.17	5.37	1.31	0.00	31.06	2.45
SM-16 [c]	90.92	8.04	1.16	------	------	------
SBnCl [c]	79.64	7.62	3.65	9.54	------	2.69
SBnI [c]	73.51	6.98	3.34	2.08	13.89	0.59 (Cl)
						1.09 (I)
SBnI [c, d]	74.10	6.89	3.37	2.23	13.98	0.62 (Cl)
						1.06 (I)

[a] P = Amberlite backbone, S = SM-16 backbone, Bn = benzyl group. [b] Batch No. 2. [c] Single analysis, all other values are averages of duplicates. [d] A second halide exchange performed on the previous entry. [e] Calculated degree of halide incorporation.

Table 2 also shows that high benzyl chloride loadings were achieved in the Amberlite system. The chloride groups were completely displaced during the Amberlite benzyl iodide preparations. The halide exchanges were readily discernible by Fourier Transform infrared (FTIR) spectroscopy in which the characteristic benzyl chloride signal at 1265 cm^{-1} was replaced by a benzyl iodide signal at 1155 cm^{-1}.

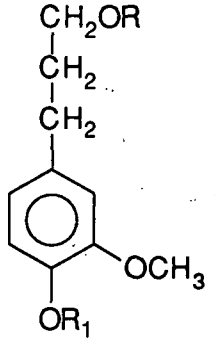
Based on x-ray analyses (SEM-EDS), the cross-sectional distribution of Cl and I in the Amberlite benzyl halides was quite homogeneous. Similar results were observed by Belfer et al.[20] The distribution is reportedly dependent upon the chloromethylation method employed.[21]

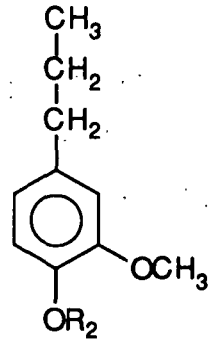
The highly crosslinked Biobead SM-16 resin did not appear to be suitable for further study primarily because of the low halide exchange yield. Highly crosslinked polymers have shown limited degrees of reactivity in other systems.[22] Unlike the SM-16, the more lightly crosslinked Amberlite XE-305 showed a high level of reactivity which should allow for the preparation of a resin with a high degree of model loading.

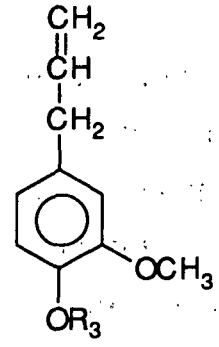
Protected Lignin Models

Preliminary work with a simple lignin model having both a propyl alcohol side chain and a phenolic hydroxyl group (**4**) was conducted to determine the conditions required to generate model-to-polymer benzyl ether linkages. As was previously encountered during the preparation of a trityl-linked model,[1] selectivity for reaction at a primary alcohol group[23] was not observed in the benzyl case. Treatment of guaiacylpropanol (**4**) with NaH/DMSO/BnBr did not give the anticipated propyloxybenzyl product **5**; rather benzylation occurred principally on the phenolic hydroxyl group (**6**). Product **6** was characterized by its acetate **7**.

This result suggested other possible protecting group methods. Guaiacylpropanol (**4**) was treated with p-methoxybenzyl iodide to give **8**; the latter was then benzylated, affording **9**. Attempts to specifically remove the p-methoxybenzyl group by treatment with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[24] led to a complicated product mixture, rather than pure **5**. Apparently, the DDQ also oxidized the electron-rich ring of the model. This was further verified by attempting unsuccessfully to cleanly deprotect the simple phenol derivative **10** to **11** with DDQ.







4, R=H, R_1=H
5, R=Bn, R_1=H
6, R=H, R_1=Bn
7, R=Ac, R_1=Bn
8, R=H, R_1=p-BnOMe
9, R=Bn, R_1=p-BnOMe
12, R=H, R_1=MEM
15, R=H, R_1=allyl
16, R=Bn, R_1=allyl

10, R_2=p-BnOMe
11, R_2=H

13, R_3=H
14, R_3=MEM

Methoxyethoxymethyl (MEM) ether was also investigated as a potential protecting group. Facile removal with trifluoroacetic acid makes the MEM ether attractive.[25] The MEM protected model **12** was prepared by first synthesizing the MEM ether of eugenol (**13**) and then hydrating **14** with diasamylborane/hydrogen peroxide. Difficulties were encountered, however, in benzylating the protected model **12** under the reflux conditions suggested by Corey et al.[25] Analysis of the product mixture revealed that the MEM group was not completely stable since some free phenol was observed. Instability was also encountered at reduced temperatures (40-50 °C) during an attempted coupling reaction with a polymer-bound benzyl halide. Milder conditions (room temperature) were not explored.

Bovee successfully used allyl groups to protect several hydroxyls on a disaccharide that was subsequently attached to a polystyrene support through a benzyl ether linkage.[2] Guaiacylpropanol was readily

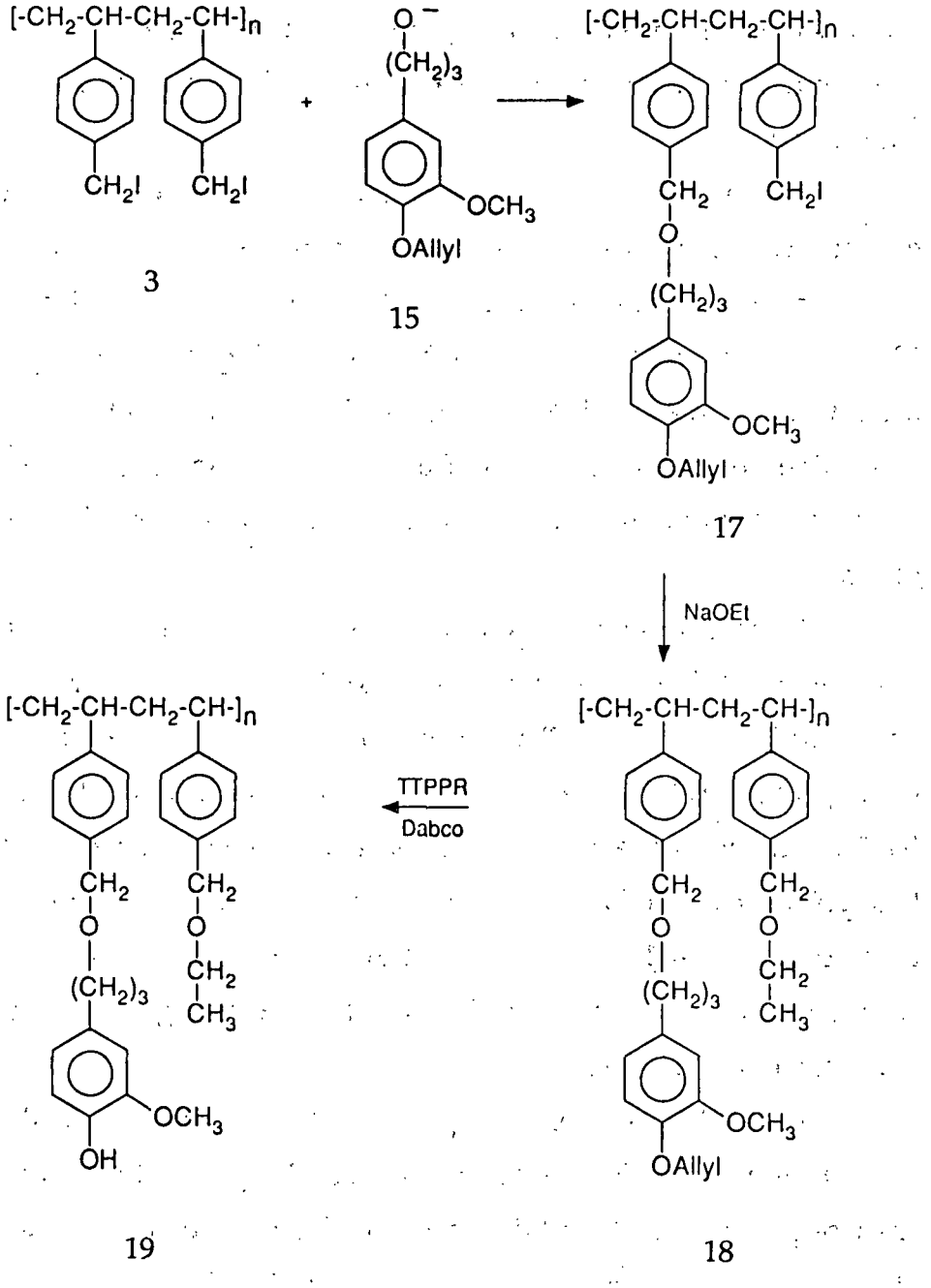
protected at the phenolic site with an equimolar amount of NaH and an excess of allylbromide to give **15**. The allyl protected model (**15**) was readily benzylated yielding **16**. The allyl group was quantitatively removed from **16** by isomerizing to a prop-1-enol with tris(triphenylphosphine)rhodium(I) chloride (TTPPR) and 1,4-diazabicyclo[2.2.2]octane (Dabco), followed by acid catalyzed hydrolysis to give **5**.[26] Complete isomerization of the phenolic allyl group required over 24 hr at reflux, compared to 6 hr for primary or secondary hydroxyls.[26-28] Allyl isomerization via potassium t-butoxide in DMSO was unsuccessful.[29] Cleavage of the prop-1-enol ethers by acetone/1M HCl was also sluggish requiring reflux conditions. Triphenylphosphine and its oxide, which were observed in the isomerization product mixture, should be easily removed in the heterogeneous case by simply washing the resin.

Thus, the allyl group appeared to possess the required protecting group qualities: selective phenolic protection, stability during benzylation, and high yield selective deprotection in the presence of a benzyl ether.

Preparation of Polymer-Bound Guaiacylpropanol

Initial attempts at coupling allyl-protected guaiacylpropanol (**15**) to the polymer-bound benzyl iodide (**3**) were performed in 25% benzene/DMF, using sodium hydride to deprotonate the primary alcohol (Scheme 2). Analysis of the resulting product (**17**) by FTIR showed strong hydroxyl and carbonyl absorbances which indicated that the DMF had sorbed onto the resin. Extended Soxhlet extraction of the resin did not remove the impurities. The coupling yield was presumably low since the FTIR spectrum did not show evidence of the allyl group.

Scheme 2


[-CH2-CH-CH2-CH-]n
CH2I
CH2I
3
O−
(CH2)3
OCH3
OAllyl
15
CH2
CH2I
O
(CH2)3
OCH3
OAllyl
17
NaOEt
TTPPR
Dabco
CH2
O
(CH2)3
CH2
O
CH2
CH3
OCH3
OH
19
18

Tetrahydrofuran, also a good swelling solvent for the resin, replaced DMF as the coupling solvent in a second attempt to bind model to the polymer. The FTIR spectrum of the coupled product (**17**) did not show any evidence of solvent absorption. An analysis of the liquor from the coupling reaction revealed starting material **15**, thus confirming that the allyl group was stable under the prescribed reaction conditions.

The loading of the coupled material was apparently much higher than in the DMF case; infrared signals at 997 and 926 cm^{-1} (=C-H bend) attested to the presence of the allyl group. The benzyl iodide FTIR signal was still evident, however, indicating that the displacement was not quantitative. A rough estimate of the model loading was determined by the weight gain of the polymer following the coupling reaction;[1] this gravimetric analysis gave 2.05 mmol of model per gram of resin.

The second step in preparing the heterogeneous model involved etherification of the remaining benzyl iodide groups. The residual benzyl iodide units (on **17**) were converted to nonreactive benzyl ethoxide groups (**18**) by treatment with sodium ethoxide in ethanol. An FTIR spectrum of the ethoxide treated resin showed that the initial benzyl iodide signal had been replaced by the corresponding benzyl ethoxide signal at 1097 cm^{-1}. Model experiments under the above reaction conditions confirmed that the allyl protecting group was stable toward sodium ethoxide.

The final step in preparing the model involved removal of the allyl group with the TTPPR/Dabco/acid hydrolysis method to generate the free phenol **19**. The FTIR spectrum of the deprotected material **19** showed a strong hydroxyl absorbance indicating that some free phenol had been produced. The allyl signals were still evident, however, sug-

gesting that the deprotection was incomplete. Two additional deprotection sequences were needed to remove the FTIR allyl absorbances.

A high resolution ^{13}C-NMR (CMR) technique[30] was also used to characterize selected resin samples (Fig. 1). The spectra, obtained using conventional methods by simply suspending the resin in $CDCl_3$, suffer from band broadening due to the heterogeneous nature of the substrate. In general, the spectra for the polymer-supported appendages were consistent with comparable soluble compounds.

The CMR spectrum of the iodomethylated polystyrene resin **3** (Fig. 1A) exhibited signals that were consistent with a polystyrene backbone.[31, 32] The signal for the heterogeneous benzyl iodide carbon, which for the soluble analog (α-iodo toluene) comes at 5.9 ppm,[33] was not readily apparent. The signal for the precursor benzyl chloride (**2**) carbon at 46 ppm was also not observed.[31, 32] This latter result confirms the elemental analysis of the iodide **3** (Table 2) in which no chlorine was detected.

Treatment of **3** with sodium ethoxide provided the corresponding ethoxymethylpolystyrene where the ethyl and benzyl signals were quite pronounced (Fig. 1B). It appears from this spectrum, and the ones which follow, that those carbons furthest removed from the polymer backbone display the strongest signal intensities. This phenomenon is related to differences in carbon relaxation times between the more motionally inhibited nuclei close to the heterogeneous support and those with more rotational freedom at the unbound end of the attached molecule.[30]

The CMR spectrum of polymer **18** (Fig. 1C) clearly showed the 4-O-allylguaiacylpropanol appendage. The allyl protecting group, which is the functional unit furthest removed from the polymer backbone, showed strong signals at 70, 117, and 135 ppm. The propyl carbons were

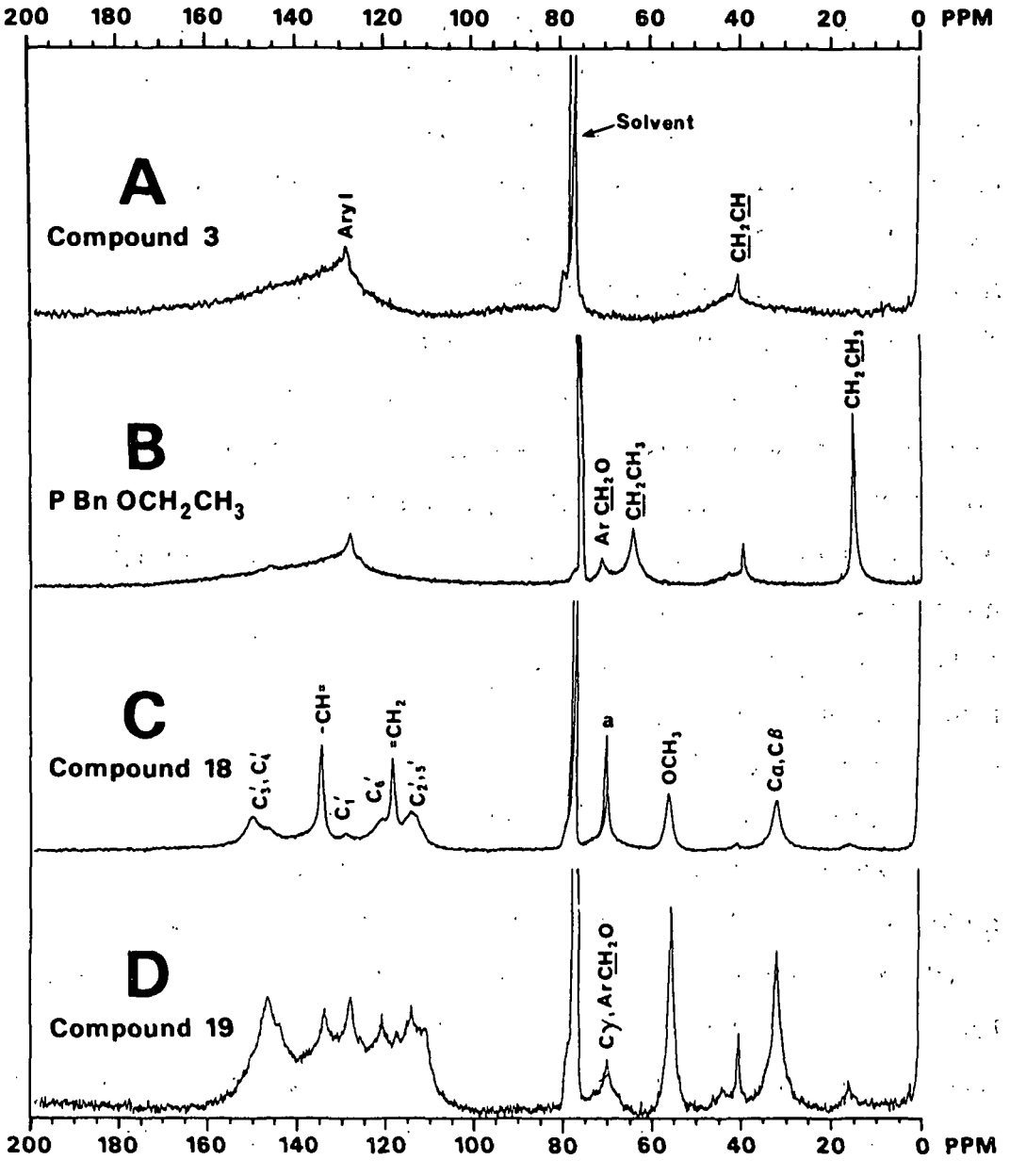


Figure 1. The ^{13}C-NMR spectra of selected resin samples; the area between 78-80 ppm represents solvent signals ($CDCl_3$). Signal "a" appears to be a combination of carbon types as described in the text.

indicated by signals at 30-35 and 70 ppm. The presence of an oxygenated aromatic ring in the resin was demonstrated by the methoxyl signal (56 ppm), together with the high field (135-150 ppm) signals for aryl-oxygen carbons and the low field (110-115 ppm) signal for aryl carbons which are ortho to aryl-oxygen substrates.

Finally, the spectrum of resin **19** (Fig. 1D), which exhibited a greater signal intensity than the other spectra, clearly showed that most of the allyl groups have been removed. Residual allyl signals were detected, however, at the resonances cited above. The oxygenated aryl ring, the methoxyl and the Cα/Cβ propyl carbons were again readily distinguished. The signals associated with the oxygenated methylenes of Cγ and the benzyl unit can not be clearly assigned; they appeared to be either part of the 70 ppm signal or overlapped with the strong solvent signal at 78-80 ppm. The relatively low signal intensity for the ethoxy groups (15 and 66 ppm) in resins **18** and **19** indicate that most of the polymer-bound benzyl iodide units were consumed by reaction with guaiacylpropanol. A fourth deprotection sequence was not attempted, since the remaining allyl groups appeared, by their inactivity, to reside in inaccessible regions of the resin.

Table 3 summarizes the elemental analysis data of each intermediate and the final product. The low iodine content of the initial coupling product (**17**) provided more evidence that model-resin coupling was extensive. The high conversion suggested that the distribution of the model was essentially that of the initial benzyl iodide. Phosphorus was detected in product **19**, indicating that a small quantity of triphenylphosphine residues had sorbed to the polymer. The phosphine residue, if covalently bonded to the resin, should be inert toward the subsequent condensation reactions.

Table 3. Elemental analysis (duplicates) of the compounds isolated during the preparation of the heterogeneous lignin model.

Substrate	C	H	O	I	P	I loading (mmol/g)
17	76.43	7.28	9.50	6.15	---	0.48
18	79.36	7.65	11.18	1.41	---	0.11
19	78.09	7.42	12.47	0.11	0.29	<0.01

Model Loading Determination

Gravimetric and elemental analysis data, along with the FTIR and ^{13}C-NMR spectra, showed that a sufficient quantity of model had been covalently bound to the polymer via a benzyl ether linkage. A method to quantify the amount of material on the resin was sought.

With the trityl-linked models, methoxyl analysis for the lignin-like units gave reproducible and quantitative results.[1] The methoxyl method was not applicable with the present benzyl-linked model since ethoxide groups, which were added to destroy the excess reactive benzyl iodide groups, are known to interfere with the determination.[34] Initially, a propyl group was investigated as an etherification reagent. Subsequent analyses with polymer-bound propoxide (no model was attached) gave positive methoxyl results; the same was found with an allyl etherified resin.

Another approach to quantification is to derivatize the polymer-bound phenol with a functional group that has an easily analyzable element. This approach was taken with heterogeneous model **19** using pentafluoropropionic anhydride and a pyridine catalyst.[35] The resulting pentafluoropropionate was found to be unstable over time giving

inconsistent results. The heterogeneous derivatization, unlike that of a soluble phenol, was shown by FTIR to be incomplete.

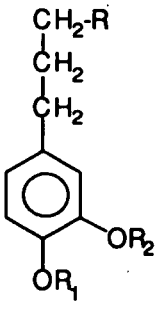
Methods for quantitatively cleaving the heterogeneous benzyl ether bond, in order to isolate and analyze the amount of guaiacylpropanol liberated, were investigated. Benzyl ethers are readily cleaved by catalytic hydrogenation.[36] This method could not, however, be implemented due to the two insoluble phases.[37] Several other reagents were tested without success. These systems included boron trifluoride with ethanethiol,[38] acetolysis,[2] and anhydrous ferric chloride with acetic anhydride.[39]

A neutral reagent, iodotrimethylsilane (ITS), reportedly cleaves benzyl ether bonds quantitatively under mild reaction conditions (room temp., 20 min).[40, 41] A similar reagent system, chlorotrimethylsilane in the presence of phenol, has been used effectively on polymer-bound substrates.[42] Tests with benzylated allylguaiacylpropanol (**16**) showed complete benzyl group removal in 20 min at room temperature. The allyl group was also cleaved but at a slower rate than the benzyl group.

Iodotrimethylsilane proved to be an effective reagent with the polymer system. Reaction of heterogeneous model **19** with ITS, followed by acetylation of the cleaved product, yielded **20**; the latter could be quantified by GLC using an internal standard.

Several minor compounds (**21-23**) were detected in the product mixture. Combined, they accounted for less than 5% of the amount of guaiacylpropanol present. The iodo compound **21** could result from two routes. The most likely prospect is that excess ITS converts the silated propyl alcohol function to the iodide after the model has been cleaved.[41, 43] The other possibility is that the model is cleaved as the iodide rather than as the alcohol. The literature reports that for soluble

models the cleavage is 100% for the benzyl iodide, giving the free alcohol.[41] This may not be the case in the heterogeneous system.



20, R=OAc, R_1=Ac, R_2=CH_3
21, R=I, R_1=Ac, R_2=CH_3
22, R=OAc, R_1=Ac, R_2=Ac
23, R=OAc, R_1=n-propyl, R_2=CH_3

The appearance of compound **22** indicated that a small amount of methyl aryl ether cleavage had occurred. Methyl ether cleavage during ITS treatment is known to be slow relative to that of the benzyl ethers and often requires harsher conditions.[44] Compound **23**, which is observed in trace quantities, is believed to result from the reduction of residual allyl groups during the course of the synthesis. The propoxy group on **23** effectively prohibits the model from undergoing condensation reactions.

The ITS procedure for quantifying the model on the resin is simple and reproducible, giving a loading of 1.29 ± 0.04 mmol/g. Quantitative results were, however, not obtained. The FTIR spectrum of ITS treated resin showed residual model; a significant benzyl iodide signal indicated, however, that a majority of the model had been displaced. In some cases, a broad signal attributable to a silyl ether was observed; the signal could be removed with concomitant generation of the corresponding alcohol by treatment with citric acid in methanol.[45]

A product of the ITS reaction, as shown by FTIR, is polymer-bound benzyl iodide. A microscopic x-ray analysis (SEM-EDS) of the ITS treated resin showed that iodine was present in the innermost regions of the bead at a uniform level, — no gradient from the outer edge of the bead was observed. The iodine distribution indicates that the macroporous regions of the resin are accessible to the ITS during the 30 min reaction period.

The nonquantitative nature of the ITS procedure suggests that not all of the bound model is accessible. The inaccessible model is presumably trapped within the microgel region of the resin. The model inaccessible to ITS would, most likely, be inaccessible to pulping liquors. Therefore, the loading value determined by the ITS method represents the amount of accessible model on the polymer support.

CONCLUSIONS

A highly functionalized polymer-bound lignin model has been prepared using a benzyl ether model-to-polymer linkage. The lignin-like monomer, guaiacylpropanol, which was attached to the support through its primary alcohol, could be selectively protected at the phenolic site by several reagents. The allyl group proved to be the best protecting group tested in terms of stability during benzylation and high yield selective deprotection in the presence of benzyl ethers.

Benzyl ether cleavage via iodotrimethylsilane was demonstrated to be a simple and reproducible method for determining the amount of accessible model (1.29 ± 0.04 mmol/g). This method was not, however, quantitative for the highly loaded resin. Analysis by an x-ray method showed that the distribution of model throughout the resin was rather homogeneous and that the interior macroporous regions of the polymer network were accessible to ITS. Spectral characterization of the

resin intermediates and products by FTIR and high resolution CMR confirmed the chemical analyses of the heterogeneous model. A highly crosslinked macroreticular resin, Biobead SM-16, showed limited synthetic reactivity and was therefore not suitable as a supporting matrix.

EXPERIMENTAL

Proton and ^{13}C-NMR were recorded on a Jeol FX100 spectrometer using TMS as an internal reference. High resolution ^{13}C-NMR spectra of the polymer-supported compounds in $CDCl_3$ were obtained by Spectral Data Services[46] on a 360 MHz instrument according to the method of Ford and coworkers.[30] Infrared spectra were recorded on a Perkin-Elmer Model 700 infrared spectrometer and standardized with polystyrene. Infrared spectra of the heterogeneous models were obtained as KBr pellets with a Nicolet 7199 Fourier Transform spectrometer. The x-ray data were recorded with a Tracor Northern TN-2000 energy dispersive spectrometer interfaced with a Jeol 35C scanning electron microscope.

Gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 5890 instrument interfaced with a Hewlett-Packard 3392 integrator. Gas chromatographic analyses were performed on a glass column (6 ft. x 2 mm ID) packed with OV-17 (3%) on Supelcoport (80-100 mesh). The general operating conditions were as follows: inj. temp. 285 °C, det. temp. (FID) 300 °C, helium carrier gas at 20 mL/min, program 100 °C (1 min) to 285 °C (5-10 min) at 10-15 degrees/min. A Hewlett-Packard 5985 instrument was used for GLC mass spectroscopy (GC/MS). The GC/MS interface was maintained at 250 °C. Electron impact (EI) MS used helium as the carrier gas, a source temp. of 200 °C, and an ionization voltage of 70 eV.

Melting points were recorded on a Thomas-Hoover capillary apparatus and are uncorrected. Elemental analyses were performed by MicroTech Laboratories, Indianapolis, IN. The methoxyl analyses of the heterogeneous models were performed by Chem-Lig International, Schofield, WI.

Amberlite XE-305 was purchased from Polysciences, Inc. Warrington, PA. The Biobead SM-16 resin was obtained from Bio-Rad Laboratories, Richmond, CA. All solvents employed, unless indicated otherwise, were A.C.S. reagent grade. Reagents and starting materials were obtained from Aldrich Chemical Co., Milwaukee, WI.

Preparations involving the use of sodium hydride (97%) incorporated anhydrous solvents and were conducted under a dry nitrogen atmosphere in oven-dried glassware until the reaction was quenched. An overhead stirring apparatus was employed in all resin modification reactions to minimize mechanical damage to the polymer support. All column chromatography purifications employed silica gel 60 (70-230 mesh ASTM) as the stationary phase.

The reactions leading to and involving the p-methoxybenzyl (**8-10**) and MEM (**12-14**) compounds are described elsewhere.[47] The unsuccessful benzyl ether cleavage and phenolic derivatization methods for determining the loading of the heterogeneous model will not be described.

Polystyrene (1) - Both the Amberlite XE-305 and Biobead SM-16 (100 g each) were washed before use with 1 L volumes of the solvents employed by Farrall and Fréchet.[48] The resins were finally rinsed in a Soxhlet apparatus with ether, then hexane for 12 hr each before being dried under reduced pressure at 60 °C.

Polymer-supported benzyl chloride (2) - Chloromethylated polystyrene (**2**) was prepared, from both the Amberlite and SM-16

resins, according to the method of Hodge and Sherrington.[12] Elemental analysis data (Table 2) and FTIR data are given in the text.

Polymer-bound benzyl iodide (3) - The iodomethylated polystyrene (3) was prepared from the chloromethylated resin **2** according to the method of Snyder.[11] The FTIR and elemental analysis data (Table 2) are given in the text. The high resolution ^{13}C-NMR spectrum of 3 (Fig. 1A) showed signals for the polystyrene backbone (**P**) that were consistent with the spectra reported by Ford et al.[31, 32] However, no signal for the benzyl iodide carbon was evident. A signal (46 ppm)[31, 32] for the benzylic carbon of the chloromethylated precursor (PBnCl) was also absent, thus confirming the FTIR and elemental analysis data which showed that the chloride units had been quantitatively displaced.

3-(3'-Methoxy-4'-hydroxyphenyl)-1-propanol (4) - Guaiacylpropanol was prepared as described by Apfeld and Dimmel.[49] After vacuum distillation, the purified material crystallized on standing to give a white solid: mp 164-165 °C.

3-(3'-Methoxy-4'-benzoxyphenyl)-1-propanol (6) - Initially, 54.4 mg (2.3 mmoles) of sodium hydride were stirred in 5 mL of DMSO. After heating at 75 °C for 5 hr, the turbid green solution was cooled to room temperature. A solution of 200 mg (1.1 moles) of guaiacylpropanol (4) in dry DMSO was added dropwise to the solution upon which the reaction mixture became yellow in color. After stirring for 15 min, 0.144 mL (1.2 mmoles) of benzyl bromide was added; the solution's color turned orange-brown. After stirring overnight, the solution was diluted with water and $CHCl_3$. The $CHCl_3$ phase was separated, washed thoroughly with water and 0.5M NaOH (to remove residual DMSO and starting phenol), dried (Na_2SO_4), and evaporated to yield 150 mg of **6**: ^{1}H-NMR ($CDCl_3$) δ 1.6-1.8 (m, 2, β-CH_2), 2.5-2.6 (m, 2,

$ArCH_2$), 3.43 (t, 2, J = 6.4 Hz, CH_2OH), 3.40 (s, 1, OH, exchangeable in D_2O), 3.75 (s, 3, OCH_3), 5.02 (s, 2, $PhCH_2O$), 6.6-7.0 (m, 3, Ar-H) and 7.2-7.4 (m, 5, Ar-H of benzyl).

The crude product (6) from above was acetylated by stirring with 0.11 mL (2 eq.) of acetic anhydride and 0.09 mL (2 eq.) of pyridine in 2 mL of $CHCl_3$ at 0 °C for 2 hr and then at room temperature for 2 hr. The reaction mixture was poured into water, and extracted with $CHCl_3$. The combined $CHCl_3$ extracts were washed successively with 3M HCl, sat. $NaHCO_3$, and water, dried (Na_2SO_4), and evaporated to give 7: ^1H-NMR ($CDCl_3$) δ 1.7-2.0 (m, 2, β-CH_2), 2.00 (s, 3, $COCH_3$), 2.5-2.6, (m, 2, $ArCH_2$), 3.75 (s, 3, OCH_3), 3.99 (t, 2, J = 6.6 Hz, CH_2OAc), 5.02 (s, 2, $PhCH_2O$), 6.6-7.0 (m, 3, Ar-H), and 7.2-7.4 (m, 5, Ar-H of benzyl). The large shift of the terminal (Cγ) methylene (3.43 to 3.99) upon acetylation established that the primary hydroxyl group had not been benzylated in the first step.

3-(3'-Methoxy-4'-allyloxyphenyl)-1-propanol (15) - Guaiacylpropanol (4) (15.8 g, 86.8 mmoles) was dissolved in 100 mL of a 50% (v/v) solution of benzene/DMF and added dropwise to a stirring mixture of sodium hydride (2.15 g, 86.8 mmoles) in 50 mL of benzene. After 30 min, 15.0 mL (174 mmoles) of distilled allyl bromide in 150 mL of benzene was added dropwise. Stirring was maintained for 10 hr after which 100 mL of 1M sodium methoxide was slowly added. After stirring for an additional 30 min, the reaction mixture was diluted with 50 mL of water and the resulting layers were separated. The organic layer was washed repeatedly with water. The aqueous washes were combined with the initial aqueous phase and then acidified with 6M HCl. The acidic solution was extracted with $CHCl_3$. The $CHCl_3$ extracts were combined with the initial organic layer and dried over Na_2SO_4. The solvent was evaporated under reduced pressure (water aspirator),

followed by evaporation under high vacuum, to remove the residual DMF. The crude product was purified by column chromatography (eluent: 25% to 75% ethyl acetate/toluene) yielding 18.2 g (94.3%) of a light gold oil: IR (cm^{-1}) 3600-3100 (OH), 995, 910 (C=C-H); ^{1}H-NMR ($CDCl_3$) δ 1.60 (s, 1, OH, exchangeable in D_2O), 1.79 (m, 2, β-CH_2), 2.65 (t, 3, J = 7.1 Hz, ArCH_2), 3.66 (t, 2, J = 6.5 Hz, CH_2OH), 3.85 (s, 3, OCH_3), 4.57 (d of t, 2, J = 5.4 and 1.5 Hz, ArOCH_2), 5.18-5.48 (d of d of q, 2, J = 16.5, 9.3, and 1.5 Hz, =CH_2), 5.89-6.27 (d of d of t, 1, J = 16.5, 9.3, and 1.5 Hz, -CH=), 6.65 (d, 1, J = 1.2 Hz, $C_{5'}$-H), 7.72 (s, 1, $C_{2'}$-H), 6.76 (d, 1, J = 1.2 Hz, $C_{6'}$-H); ^{13}C-NMR ($CDCl_3$) ppm 31.6 (t, ArCH_2), 34.2 (t, β-CH_2), 55.8 (q, OCH_3), 61.9 (t, CH_2OH), 70.0 (t, ArOCH_2), 112.2 (d, $C_{2'}$), 113.7 (d, $C_{5'}$), 117.4 (t, =CH_2), 120.0 (d, $C_{6'}$), 133.4 (s, $C_{1'}$), 134.8 (d, -CH=), 145.9 (s, $C_{4'}$), 149.1 (s, $C_{3'}$); MS z/e (relative intensity) 222 (68, M^+), 181 (72), 164 (12), 163 (100), 137 (18), 135 (17), 121 (10), 107 (43), 105 (17), 103 (27), 91 (28), 79 (18), 78 (11), 77 (24), 65 (11), 41 (11), 39 (11).

Anal. calcd. for $C_{13}H_{18}O_3$ (%): C, 70.2; H, 8.2; O, 21.6. Found: C, 70.5; H, 8.1; O, 21.6.

3-(3'-Methoxy-4'-allyloxyphenyl)-1-benzyloxypropane (16) - To a stirring mixture of 0.33 g (14 mmoles) of sodium hydride in 15 mL of DMF was added, via a dropping funnel, 2.00 g (9.0 mmoles) of allyl-protected guaiacylpropanol (**15**) dissolved in 20 mL DMF. After the reaction mixture had stirred for 1 hr, 4.28 mL (36.0 mmol) of benzyl bromide was added. Stirring continued for 5 days, after which methanol (20 mL) was slowly added, followed by 40 mL of water. The resulting solution was extracted with $CHCl_3$ which was subsequently removed under reduced pressure. Residual DMF was evaporated from the remaining organic phase under high vacuum. The crude product was purified by column chromatography (eluent: dichloromethane) yielding 1.81 g (64.4%) of a light yellow oil: IR (cm^{-1}) OH signal absent;

^{1}H-NMR (d_6-DMSO) δ 1.68-1.96 (m, 2, β-CH_2), 2.50 (t, 2, J = 7.6 Hz, $ArCH_2$), 3.43 (t, 2, J = 6.4 Hz, CH_2OBn), 3.73 (s, 3, OCH_3), 4.45-4.52 (m, 4, $BnCH_2O$, $ArOCH_2$), 5.13-5.46 (d of d of q, 2, J = 17.3, 10.3, and 1.5 Hz, $=CH_2$), 5.84-6.22 (d of d of t, 1, J = 17.3, 10.3 and 1.5 Hz, -CH=), 6.60-6.88 (m, 3, Ar-H), 7.32 (s, 5, Ar-H of benzyl); ^{13}C-NMR (d_6-DMSO) ppm 31.0 (t, $ArCH_2$), 31.3 (t, β-CH_2), 55.4 (q, OCH_3), 68.9 (t, CH_2OH), 69.2 (t, $ArOCH_2$), 71.7 (t, $BnCH_2O$), 112.5 (d, $C_{2'}$), 113.9 (d, $C_{5'}$), 116.7 (t, $=CH_2$), 119.8 (d, $C_{6'}$), 126.9 (d, C_4 of benzyl), 127.0 (d, $C_{3,5}$ of benzyl), 127.8 (d, $C_{2,6}$ of benzyl), 133.8 (s, $C_{1'}$), 134.5 (d, -CH=), 138.4 (s, C_1 of benzyl), 145.6 (s, $C_{4'}$), 148.9 (s, $C_{3'}$); MS z/e (rel. int.) 312 (20, M^+), 221 (5), 177 (5), 137 (7), 92 (8), 91 (100), 77 (5), 65 (6).

3-(3'-Methoxy-4'-hydroxyphenyl)-1-benzoxypropane (5) - In 50 mL of an ethanol/benzene/water (7:3:1 v/v) mixture was dissolved 0.51 g (15 eq.) of the starting compound (**16**) along with catalytic amounts of tris(triphenylphosphine)rhodium(I) chloride (0.10 g, 1 eq.) and 0.05 g (4 eq.) of 1,4-diazobicyclo[2.2.2]octane. The mixture was refluxed for 24 hr and then cooled. Water (25 mL) was added and the reaction mixture extracted with $CHCl_3$. The extracts were concentrated under reduced pressure and then dissolved in 60 mL of acetone/1M HCl (9:1 v/v). After refluxing for 1.5 hr, the reaction mixture was cooled, diluted with 50 mL of water, and extracted with $CHCl_3$. The combined $CHCl_3$ extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. A GLC analysis of the product mixture indicated that the allyl deprotection was incomplete. The two procedures were repeated to achieve complete conversion. The crude product, a dark oil, was purified by column chromatography (eluent: 10% ethyl acetate/toluene) yielding a light yellow oil: MS z/e (rel. int.): 272 (71, M^+), 181 (40), 164 (27), 151 (49), 137 (100), 122 (13), 119 (23), 119 (23), 91 (77), 77 (18), 65 (15).

Polymer-supported 4-O-allylguaiacylpropanol (17) - Allyl-protected guaiacylpropanol (**15**) (4.25 g, 19.1 mmoles) was dissolved in 50 mL of THF and added dropwise to 0.46 g (18.9 mmoles) of sodium hydride slurried in 25 mL of THF. The resulting mixture was stirred (overhead) for 60 min. Polymer-bound benzyl iodide (6.00 g, 14.7 mmoles) was then added to the reaction flask. Stirring continued for 114 hr, after which the resin was isolated in two batches by filtration and washed with 3x200 mL of THF each. The resin was further washed in a Soxhlet apparatus with THF followed by hexane for 12 and 11 hr, respectively. A yield of 7.03 g of coupled material (**17**) was obtained after the resin had dried in vacuo at 40 °C. Reported yields are approximate values due to static losses on transferring operations. The FTIR spectrum of **17** exhibited signals assigned to the bound guaiacylpropanol appendage at 1262 and 1229 (Ar-O-R), 1141 and 1101 (R-O-R), and at 997 and 926 (allyl =C-H) cm^{-1}. Signals at 1512 (Ar C=C) and 1419 (-CH_2-) cm^{-1}, which were also attributed to the bound model, were enhanced relative to those observed in the spectrum of the precursor benzyl iodide (**3**). The elemental analysis data (Table 3) for compounds **17-19** are discussed in the text.

A sample of the reaction liquor was taken to dryness under reduced pressure. The residue was dissolved in $CHCl_3$, diluted with an equal volume of water, and acidified with 6M HCl. The organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated under vacuum. A GLC analysis of the resulting solution revealed the presence of unmodified soluble model (**15**), thus confirming that the allyl group is stable under the specified coupling reaction conditions.

Polymer-supported 4-O-allylguaiacylpropanol/ethoxide (18) - The unreacted benzyl iodide units from the coupling reaction were converted into nonreactive benzyl ethoxide groups. The coupled

material (**17**) (6.75 g) was slurried under nitrogen in 35 mL of THF to which an excess (165 mL) of 0.8M sodium ethoxide in ethanol was added. The reaction mixture was stirred for 103 hr after which the resin was isolated by filtration. Washings were conducted with 6x100 mL portions of methanol, acetone, and THF. The resin product (**18**) was dried at 40 °C under reduced pressure, after being rinsed in a Soxhlet apparatus with hexane for 6.5 hr. A yield of 6.37 g was isolated. The polystyrene backbone signals in the high resolution ^{13}C-NMR spectrum of **18** were weak (Fig. 1C) but remained consistent with those reported by Ford.[31, 32] The benzyl ethoxide signals (15.8 ppm, BnO-$CH_2\underline{CH_3}$; and 65.6 ppm, BnO$\underline{CH_2}CH_3$) were also weak relative to the signals from the supported model. Weak benzyl ethoxide signals are consistent with the FTIR and elemental analysis data which indicated that the ethoxide loading was low due to an initially high displacement of iodide groups during the coupling reaction. Broad signals due to the supported model were observed as follows: ($CDCl_3$) ppm 31.8 ($ArCH_2$ and β-CH_2), 55.9 (OCH_3), 70.0 (PCH_2O, CH_2OBnP, and $ArOCH_2$), 113.5 (C_2 and C_5), 117.7 (=CH_2), 120.6 (C_6), 133.8 (C_1 and -CH=), 150.3 (C_4 and C_3).

Polymer-supported guaiacylpropanol/ethoxide (19) - The allyl protecting group was removed from the phenolic site of the bound model as follows. Tris(triphenylphosphine)rhodium(I) chloride (1.15 g, 1.25 mmoles) and 0.51 g (0.45 mmoles) of 1,4-diazabicyclo[2.2.2]octane were dissolved in 275 mL of a warm ethanol (absolute)/benzene/water (7:3:1 v/v) solution. The ethoxide treated resin (**18**) (5.38 g) was added and the reaction mixture gently refluxed for 9.5 hr. Once cool, the resin was isolated by filtration and washed (5x100 mL) with $CHCl_3$, THF, and hexane before being dried under reduced pressure at 40 °C. The resin, which now supported the isomerized protecting group, was suspended

in a mixture of 1.2M HCl (35 mL) and acetone (175 mL). After gently refluxing for 4 hr, the reaction mixture was allowed to cool. The resin was filtered and washed (5x100 mL) with acetone, THF, and hexane. The allyl deprotection sequence was repeated twice more. On the third trial, the acid reflux was extended to 6 hr. The final product was washed in a Soxhlet apparatus for 6 hr with hexane before being dried in a vacuum oven at 40 °C. The isolated yield of **19** was 4.86 g. High resolution ^{13}C-NMR signals for the supported model **19** (Fig. 1D) were observed as follows: ($CDCl_3$) ppm 31.8 ($ArCH_2$ and β-CH_2), 55.8 (OCH_3), 70.0 (PCH_2O and CH_2OBnP), 111.2 (C_2), 114.3 (C_5), 121.0 (C_6), 133.8 (C_1), 143.8 (C_4), 146.6 (C_3). The signals at 70.0 ($ArOCH_2$), 117.8 ($=CH_2$), and 133.8 (-CH=) were greatly reduced in relative area (vs. the spectrum of **18**) indicating that a substantial portion of the allyl groups were removed.

Polymer-bound benzyl ethoxide - Under a continuous stream of nitrogen, 2.50 g (6.13 mmol) of dried polymer-bound benzyl iodide was stirred (overhead) for 112 hr in 16 mL of freshly distilled THF and an excess (64 mL) of 0.9M sodium ethoxide in ethanol. The reacted resin was isolated by filtration and washed with 6x50 mL of methanol, acetone, and THF. The product was then extracted with hexane for 8 hr and dried under reduced pressure at 40 °C. Elemental analysis showed a residual iodide content of 0.21 mmol/g. To reduce the level of remaining iodide, a second ethoxide treatment was conducted for 76 hr in an analogous manner. The FTIR spectrum of the final product showed a strong signal at 1098 cm^{-1} (C-O str.) in place of the original benzyl iodide signal at 1155 cm^{-1}. Elemental analysis gave the following: C, 82.1; H, 8.3; O, 8.7; I, 1.1 (0.09 mmol iodide per gram of resin). The ensuing assignments were made for the observed signals in the high resolution ^{13}C-NMR spectrum (Fig. 1B) of the polymer-bound

benzyl ethoxide: ^{13}C-NMR ($CDCl_3$) ppm 15.4 (CH_3), 40.5 (backbone methine),[31, 32] 38-47 (backbone methylene), 65.6 (OCH_2), 72.8 ($ArCH_2O$), 126.5 (C_4), 128.3 ($C_{2,3,5,6}$), 146.2 (C_1).

Polymer-supported propoxide - Sodium propoxide was prepared by dissolving freshly cut sodium metal in 1-propanol under a nitrogen atmosphere. Polymer-supported propoxide was prepared by stirring 1.00 g (3.09 mmoles) of polymer-bound benzyl iodide in 40 mL of 1M sodium propoxide in propanol and 15 mL of dry DMF for three days. The resin was isolated by filtration and washed successively with methanol and acetone (4x100 mL) followed by THF and hexane (3x 100 mL). The washed resin was dried in a vacuum oven at 40 °C. An aliphatic ether stretch signal at 1097 cm^{-1} was observed in the FTIR spectrum along with additional C-H stretch signals at 2961 and 2878 cm^{-1}. An iodine loading of 0.35 mmol/g remained on the resin; a methoxyl content of 7.81% was also observed. The positive test for methoxyl units confirms that the propoxide group, and the allyl group as shown below, interfere with the methoxyl determination.

Polymer-supported allyloxide - The polymer-supported allyloxide was prepared in an analogous manner to the heterogeneous propoxide. The FTIR spectrum showed characteristic signals at 1097 (C-O str.), 991 and 923 (C=C-H str.) cm^{-1}. The resin had a methoxyl content of 5.73%.

Heterogeneous model loading by iodotrimethylsilane (ITS) - Under a nitrogen atmosphere, 1.00 mL of dry acetonitrile was added to a dark vial containing 20-25 mg of the dry heterogeneous model (**19**). After the resin had soaked for 15 min, 0.035-0.040 mL (approx. 1.5-2.0 eq. per oxygen atom) of ITS was added to the vial via syringe. The vial was sealed and shaken occasionally over a 30 min period. The reaction was quenched by adding 0.50-0.75 mL of anhydrous methanol containing

internal standard (4-ethoxyphenol). The reaction liquor was pipetted from the beads and added to 0.25 mL of pyridine. The resulting solution, along with 3x1 mL methanol rinses of the reacted resin, was concentrated under reduced pressure at a maximum of 40 °C. Pyridine (0.50 mL), acetic anhydride (0.75 mL), and anhydrous sodium acetate (30 mg) were then added to the resulting residue. After shaking for 24 hr, the acetylation mixture was treated with 4x2.5 mL aliquots of cold water and extracted with 2x5 mL of CH_2Cl_2. The organic extract was washed with 5 mL of 1M HCl followed by 3x5 mL of water, then dried (Na_2SO_4), and concentrated under reduced pressure with no applied heat. The residual material was dissolved in 2 mL of CH_2Cl_2, stored in a dark vial over Na_2SO_4, and analyzed by GLC. The MS, z/e (rel. int.), for the compounds **(20-23)** observed in the ITS product mixture were as follows: **3-(3'-methoxy-4'-acetoxyphenyl-1-acetoxypropane (20)**, 266 (12, M^+), 224 (83), 164 (100), 149 (40), 137 (79), 133 (25), 132 (22), 131 (15), 122 (10), 107 (10), 91 (15), 77 (11), 43 (28); **3-(3'-methoxy-4'-acetoxyphenyl)-1-iodopropane (21)**, 334 (5, M^+), 292 (62), 155 (10), 137 (100), 43 (8); **3-(3',4'-diacetoxyphenyl)-1-acetoxypropane (22)**, 294 (6, M^+), 252 (29), 210 (94), 150 (100), 149 (19), 133 (10), 132 (19), 131 (9), 123 (29), 122 (16), 91 (10), 77 (14), 43 (93); **3-(3'-methoxy-4'-propoxyphenyl)-1-acetoxypropane (23)**, 266 (84, M^+), 206 (6), 179 (7), 164 (94), 163 (19), 149 (34), 137 (100), 133 (28), 132 (18), 131 (18), 91 (20), 77 (18), 43 (57).

A loading value of 1.29 ± 0.04 mmol/g was obtained employing the conditions cited above. Increasing the reaction time to 90 min or the number of ITS equivalents (to approx. 5) lowered the loading values to 1.21 and 1.16 mmol/g, respectively. Raising the reaction temperature to 70 °C had a pronounced adverse effect as the loading level was reduced to 0.15 mmol/g. A loading of 1.35 ± 0.05 mmol/g was obtained by replacing acetonitrile with carbon tetrachloride. Use of

carbon tetrachloride was not continued since the suspended beads tended to cling out of solution onto the walls of the vial. It was felt that the reproducibility over multiple samples would not be as high as the initial tests indicated.

The reacted resin was isolated by filtration and washed with 5x2 mL aliquots of the following solvents: methanol, ether, pet. ether, and hexane. The resin was dried in a vacuum oven at 40 °C before being analyzed by FTIR.

A portion (10 mg) of the isolated ITS treated resin was powdered and shaken for 3.5 hr in 2 mL of 1M citric acid monohydrate in methanol.[45] The resin was isolated by filtration and washed with the solvents used in the above isolation procedure. The FTIR spectrum was discussed in the text.

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ADDENDUM

Paper number two in this series (see reference 1) contained an error in Table 2. The column heading "Kraft-147 °C" should read "Soda-147 °C"; likewise, the heading "Soda-147 °C" should read "Kraft-147 °C". This correction does not affect the conclusions drawn from Table 2.

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